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TITLE OF THE INVENTION (900 characters max)					
METHOD FOR REPLICATING SINGLE WALLED CARBON NANOTUBES USING CHEMICAL ATTACHMENT OF CATALYST PRECURSORS					
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Respectfully submitted,

(Page 1 of 2)

Date July 12, 2004

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A METHOD FOR REPLICATING SINGLE WALLED CARBON NANOTUBES USING CHEMICAL ATTACHMENT OF CATALYST PRECURSORS

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates generally to single walled carbon nanotubes (SWNTs), and more specifically to growing SWNTs from pre-grown SWNT seeds and a catalyst.

Background of the Invention

Nanoparticles have been increasingly studied due to their physical and chemical properties. Fullerenes are a class of carbon-based nanoparticle that are broadly defined as the third crystalline form of the element carbon after diamond and graphite. Fullerenes are molecular solids that consist of predominantly fused six-membered and five-membered rings. Two general types of fullerenes may be described: Buckyballs and carbon nanotubes. Buckyballs have spherical structures and are typified by C_{60} . Other spherical fullerenes include C_{70} and higher oligomers. Single walled carbon nanotubes (SWNTs) are elongated members of the fullerene family.

The interior cavity of a fullerene can accommodate an atom, molecule, or particle, depending on the volume circumscribed by the structure of the fullerene, to provide so-called doped fullerenes. Furthermore, reacting the surface, under suitable conditions to form either covalent, Van der Waals or dipolar interactions with a chemical substituent, may chemically functionalize fullerenes.

SWNTs have come under intense multidisciplinary study because of their unique physical and chemical properties and their possible applications. The electronic characteristics of SWNT can be described as metallic or semiconducting; such characteristics deriving from the helicity and diameter of the SWNT (Bachilo, et al. *Science* 2002, 298, 2361). The type of nanotube can be defined by two integers, "n" and "m." The (n,m) of a carbon nanotube describes the roll-up vector of a graphene sheet, diameter of the tube this sheet produces, and the electronic bandgap of such nanotubes are correlatable with this vector. When $n = m$, the nanotube has a 0 eV bandgap and is therefore a metal-like conductor at room temperature, and these have further been referred to as the armchair tubes. When the difference of n and m is a multiple of 3, then a semi-metallic species is generated with a bangap of on the order of milli-eV. If the difference of n and m is not a multiple of 3 or the quantity 0, then the nanotube is a semiconductor with a bandgap $\sim 1-2$ eV. Such properties make SWNTs ideal for nanoscale electronic, optoelectronic, and sensing materials.

Nanotube field effect transistors (FETs), for example, have already been demonstrated and the ability of the armchair configuration to conduct electricity offers potential for low loss electrical power grid.

A further major obstacle to such efforts has been diversity of tube diameters, chiral angles, and aggregation states (often termed bundling or roping) of the tubes. Aggregation is particularly problematic because highly polarizable, smooth sided SWNTs readily form bundles or ropes with van der Waals binding energy of ca. 500 eV per nanometer of tube contact. This bundling perturbs the electronic structure of the tubes and precludes the separation of SWNTs by size or type. The diversity of tube diameters/chiral angles means that in order for several applications to be realized either a method for separating SWNTs by type or the specific synthesis of individual SWNT types must be developed. Since separation would be performed after each synthesis of mixed diameters/chiralities, it will be more efficient for any commercial process to be able to synthesize particular diameters/chiralities. Presently, there are no known methods for doing this directly from the ordinary feedstocks used in SWNT synthesis (such as methane and CO). However, if a suitable catalyst could be chemically bound to a small length of an individual SWNT, and that SWNT grown in length with retained diameter/chirality then large samples of specific SWNTs may be produced. Such a process is termed "cloning." The term cloning is used herein to describe the growth of a longer SWNT from a pre-formed shorter SWNT such that the diameter/chirality is maintained.

SWNTs may be grown by any known technique. Such techniques include, but are not limited to, growing SWNTs from CO and/or hydrocarbon sources using transition metal (TM) catalysts. See Nikolaev et al., *Chem. Phys. Lett.*, **1999**, *313*, 91-97; Bronikowski et al., *J. Vac. Sci. Technol. A: Vac. Surf. Films*, **2001**, *19*, 1800-1805. These catalysts include, but are not limited to, particles of iron, molybdenum, chromium, nickel, and their alloys.

Mueller and co-workers have reported the synthesis of a large molybdenum-iron-oxide based cluster having the formula $[H_xPMo_{12}O_{40}CH_4Mo_{72}Fe_{30}(O_2CMe)_{15}O_{254}(H_2O)_{98}]$, hereafter referred to as "FeMoC" (Mueller et al., *Angew. Chem., Int. Ed.*, **2000**, *39*, 3414). This compound decomposes upon thermolysis to yield an alloy that has been shown to be useful as a catalyst for the growth of SWNTs.

If an individual SWNT is to be cloned then there are several problems that must be overcome. Most importantly, a suitable catalyst must be bound directly to the SWNT in question. Excess catalyst cannot be present since this will allow for growth of new SWNTs with no control over diameter/chirality. An additional requirement is that the catalyst be bound on the end of the SWNTs rather attached to the side wall, however, the catalyst may react with the side wall allowing the formation of two new ends. Additional requirements are that the complex between the transition metal (TM) catalyst and the SWNT must be stable to solvents and handling, and that the

catalyst be of a consistent composition such that growth rates may be controlled for each SWNT. It is desirable that catalytic growth of the SWNT occurs under heterogeneous conditions on a surface of a solid support. The TM catalyst or catalyst precursor and the SWNT should therefore be attached to a suitable catalyst support via chemical or physical means. To date there has been no efficient way to achieve these goals. The present invention provides a method and composition to create suitable catalyst-SWNT components of a cloning or replicating reaction.

SUMMARY

The present invention addresses the above and other needs in the art by providing methods of making a composition of matter comprising the reaction product of SWNT that has been functionalized to allow chemical bonding to a transition metal (TM) cluster and a TM cluster with complementary functional groups, and the application of this composition of matter to the cloning of SWNTs.

In some embodiments, the present invention includes a chemically functionalized SWNT via the protection of the sidewalls (and creation of individual tubes) prior to providing functional groups to allow reaction with the TM cluster. These sidewall functional groups are non-reactive with the TM cluster and may be readily removed during the step to convert the TM cluster to its catalytically active form and/or under the conditions used to grow the SWNTs.

In some embodiments, the present invention includes the formation of functional groups on the ends of the SWNT comprising carboxylate (or carboxyl) groups formed by treatment with hydrogen peroxide and sulfuric acid.

In some embodiments, the present invention includes the formation of functional groups on the ends of the SWNT comprising quinone groups formed by treatment with sulfuric and nitric acids.

In some embodiments, the present invention includes the formation functional groups on the ends of the SWNT comprising thiol groups, for example, oxalyl chloride or thionyl chloride (to afford the terminal acid chloride functionalities) followed by reaction with α,ω -dithiols such as benzene-1,4-dithiol or 1,8-octanedithiol, etc.

In some embodiments, the present invention includes a formulation wherein the TM cluster is a precursor to a TM catalyst or TM alloy catalyst for the growth of SWNTs.

In some embodiments, the present invention includes the use of a TM oxide cluster that may be converted to a catalyst upon reaction or thermolysis.

In some embodiments, the present invention includes the use of the TM cluster with the formula $[H_xPMo_{12}O_{40}CH_4Mo_{72}Fe_{30}(O_2CMe)_{15}O_{254}(H_2O)_{98}]$ (FeMoC) that is prepared by the reaction of $H_3[P(Mo_2O_{10})_4]$ with $FeCl_2$, Na_2MoO_4 and $MeCO_2H$.

In some embodiments, the present invention includes the purification and activation of the TM cluster by washing with water and soxhlet extraction with EtOH. The latter step activates the surface of the FeMoC to reaction with SWNTs by replacing bound water with easily removed EtOH ligands to yield FeMoC(EtOH).

In some embodiments, the present invention includes the reaction of FeMoC(EtOH) with carboxylate derivatized SWNTs in $CHCl_3$ solution at 50°C results in the formation of a new composition of matter comprising FeMoC chemically bound to the ends of the SWNTs.

In some embodiments, the present invention includes the conversion of the TM cluster to a TM catalyst particle bound to the end of a SWNT.

In some embodiments, the present invention includes the use of the TM catalyst particle bound to the end of a SWNT for the growth of SWNTs. Note that the reactivities of SWNTs of differing chirality may vary widely.

In another embodiment, the present invention includes attaching the TM or TM-alloy catalyst or catalyst precursor particle to a catalyst support prior to reaction with the SWNT.

In another embodiment, the present invention includes attaching the product of the reaction of the SWNT with the TM or TM-alloy catalyst particle to a catalyst support.

It will therefore be seen that a technical advantage of the present invention includes an improved method for the specific attachment of an individual catalyst particle to a single SWNT. Further advantages include the purification and activation of the TM catalyst precursor to promote reaction with functionalized SWNT.

The foregoing has outlined rather broadly the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter that form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and the specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more detailed description of the embodiments of the present invention, reference will be made to the accompanying drawings, wherein:

FIGURE 1 illustrates the structure of the FeMoC complex;

FIGURE 2 illustrates, schematically, the attachment of FeMoC to the end of a SWNT (Step 1), the deposition of the SWNT-FeMoC complex on a surface (Step 2), the reductive docking of the FeMoC complex with the SWNT (Step 3), and growth of the SWNT of Step 3 under growth conditions (step 4); and

FIGURES 3 A and B depict AFM images of SWNTs with FeMoC attached to their ends.

DETAILED DESCRIPTION

Applicants have discovered that TM catalyzed SWNTs may be grown using a TM catalyst that is attached to SWNTs. The present invention is directed to SWNT-TM complex composites, and to methods of using such complexes in the further growth and cloning of SWNTs.

A catalyst is ordinarily defined as an element, compound, alloy or mixture that increases the rate of a reaction. In the present invention the term TM catalyst (TMC) is to mean an element, compound, mixture or alloy comprising at least one transition metal that will act as a catalyst for a chemical reaction. In addition, the term TM catalyst includes catalyst precursors, which may be an element, compound, mixture or alloy that undergoes a reaction before becoming active as a catalyst.

Without being limited by theory, it is believed that providing a reactive group on the ends of a SWNT that is designed to allow specific attachment of a TM catalyst facilitates the growth of the SWNT with the same chirality and/or diameter of the original SWNT; the original *n* and *m* parameters in the nanotube acting as a template for dictating the *n* and *m* parameters in the further nanotube growth.

Method of Activating the Ends of a SWNT

There are numerous known methods for the activation of the ends of SWNTs to allow further reaction. However, with respect to the present invention, it is important that the terminus be chosen from a chemical group that will allow for binding to the TMC. The TMC may be a transition metal catalyst precursor or transition metal cluster or a transition metal fragment that can be further reacted to create a transition metal catalyst precursor. Suitable active groups include, but are not limited to, carboxylate or carboxyl groups, thiols, pyridine, amines, and ketones. The identity of the functional group is chosen to match the chemistry of the TMC and to optimize the specific nature of the SWNT-TMC interaction. The functional group may be chosen to react with the TM cluster or catalyst precursor by covalent bonding, Lewis acid-base interactions, hydrogen bonding, ionic forces, van der Waal forces, or combinations thereof. Preferably the interaction between the SWNT and the TM cluster or TM catalyst precursor should be a strong interaction involving covalent and/or donor bonding.

Purified carbon nanotubes may be treated with piranha to give carboxylic acid terminated carbon nanotubes (Liu et al., *Science*, 1998, 280, 1253). The piranha treatment is a mixture of hydrogen peroxide (H₂O₂) and concentrated sulfuric acid (H₂SO₄). The piranha treated carbon nanotubes are then suspended in water that is facilitated by surfactants. The nanotubes, surfactants and water are added together then homogenized, sonicated, and centrifuged (O'Connell et al., *Science* 2002, 297, 593). This gives carbon nanotubes that are dispersed in water predominately

as individuals; the tubes no longer remain roped or bundled. Therefore discrete tube types (n and m) can be freed from all their neighboring tubes through this surfactant-wrapping protocol.

As an alternative to the piranha treatment, SWNTs may be reacted with a suitable reagent to produce alternative functional groups on the end of the SWNTs. Quinone functional groups are thought to form by the treatment of SWNTs with sulfuric and nitric acids, and the newly derived carbonyl functionalities can be addressed with TMCs bearing bearing carbonyl-binding groups such as primary amines (to form imines emanating from the nanotube ends). As a further alternative, the piranha-treated SWNTs may be further reacted to give active substituents such as a thiol.

Method of Protecting the Side Walls of a SWNT

There are numerous known methods for the functionalization of the sidewalls of SWNTs. However, with respect to the present invention it is important that the functionalization be chosen such that the sidewalls are not available for reaction or binding to the TM cluster or TM catalyst precursor and such that removal of the surfact wrapping does not cause the nanotubes to re-rope. For an overview of this protocol, see: Dyke, C. A.; Tour, J. M. "Overcoming the Insolubility of Carbon Nanotubes through High Degrees of Sidewall Functionalization," *Chem. Eur. J.* **2004**, *10*, 812-817. Suitable protective groups include, but are not limited to, halogen, nitro, cyano, alkyl, aryl, arylalkyl, carboxylic ester, thiocarbonate, sulfonate, amide, alkoxy, polyether, and combinations thereof. The functional group may be chosen to be inert to the TM cluster or catalyst precursor with regard strong interactions.

A further function of the sidewall protection is to prevent bundling of the SWNTs, and to allow manipulation of the nanotubes as individuals as opposed to bundles (or ropes). The ability to manipulate carbon nanotubes as individuals is crucial for cloning one particular type of nanotube.

A further function of the sidewall protection is to allow for the SWNTs to be soluble in a solvent suitable for reaction with the TM cluster or TM catalyst precursor.

Diazonium chemistry is employed to place substituted aryl moieties on the sidewall of carbon nanotubes. Surfactant wrapped SWNTs are reacted with a suitable diazonium compound in an aqueous solution. See Dyke et al., *Nano Letters*, 2003, *3*, 1215.

The sidewall protection of the SWNT does not have to employ the formation of covalently bound substituents. The sidewalls of the SWNT may be protected from reaction with the TMC by alternative means, such as surrounding or encapsulating the SWNT in a surfactant, polymer or biopolymer.

Method of Purifying and Activating the TM Catalyst to Allow Reaction with the SWNT

It is important that each catalyst particle that is attached to a SWNT have an identical composition. Significant variation in composition may result in variations in growth rate during the cloning process. In this regard the purification of the TM cluster or TM catalyst precursor is important.

Purifying the TM cluster or TM catalyst precursor may be accomplished by a number of methods, including crystallization, sublimation, and/or filtration. However, in addition to purification it is desirable to activate the TM cluster or TM catalyst precursor towards reaction with the activated SWNTs. Furthermore, for the cloning of SWNTs to be commercially viable, large quantities of the catalyst must be prepared.

One such suitable TM cluster is $[H_xPMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(O_2CMe)_{15}O_{254}(H_2O)_{98}]$ (FeMoC), the structure of which is shown in FIGURE 1. As reported the synthesis of FeMoC is a low yield process that requires slow evaporation for several days. See Mueller et al., *Angew. Chem., Int. Ed.*, 2000, 39, 3414. This is highly inefficient and the reaction product shows variable composition. FeMoC consists of two components, a central Keggin ion $[H_xPMo_{12}O_{40}]^{n-}$, and a surrounding keplerate cage $[H_4Mo_{72}Fe_{30}(O_2CMe)_{15}O_{254}(H_2O)_{98}]$. The Keggin ion is blue and soluble in water; the keplerate cage is yellow with low solubility in water; FeMoC is green. Based upon the known method of purification, it is common for quantities of the keplerate cage to contaminate the FeMoC samples. Such contamination will alter the Fe:Mo ratio of the resulting in a potential variation in catalyst activity and growth rate. In addition, the FeMoC is insoluble in most solvents that it does not react with, and shows slow reaction with suitable functional groups. This is in part due to the presence of coordinated water on the surface of the FeMoC.

In order to prepare FeMoC on a large scale, a simpler purification procedure and a chemical alteration of the FeMoC was developed to allow for its ready reaction with functionalized SWNTs.

Whereas the known chemistry of FeMoC suggests that the FeMoC may be purified by its precipitation from water solution, Applicants have found, surprisingly, that a significant additional yield may be obtained by the following protocol. The crude FeMoC reaction mixture prepared by the reaction of $H_3[P(Mo_2O_{10})_4]$ with $FeCl_2$, Na_2MoO_4 and $MeCO_2H$ is reduced to dryness. The resulting solid is washed with water to remove the blue Keggin ion to yield a pale green solid that is insoluble in neutral water. The pale green solid is extracted into EtOH using a Soxhlet extraction apparatus. Whereas a typical extraction will yield a dilute solution, Soxhlet extraction results in a concentrated solution of a modified FeMoC. Thermogravimetric and mass spectral analysis show that the modification results from the substitution of approximately thirty water ligands for an equal number of EtOH ligands. The activated FeMoC has a solubility of approximately 12 mg per cm^3 in EtOH.

A further advantage of this method of purification is that the EtOH ligands are much easier to remove from the coordination sphere of the FeMoC than the coordinated water ligands. Thus subsequent reactions with the activated SWNTs are possible and enabled. The EtOH ligands are readily displaced by ligands containing suitable substituents such as carboxylate groups, thiols, and pyridines. The extent of the substitution is dependent on the relative strength and binding constant of the ligand.

A further alternative to the use of an easily displaced ligand is the functionalization of the outer surface of FeMoC clusters with molecular linkers to the SWNT. In a typical example, FeMoC may be activated by reaction with 2-aminoethanethiol hydrochloride (2-AET-HCl). The resulting activated FeMoC can react with carboxylate functionalized SWNTs. Alternative ligands include those based upon other carboxylic acids (including benzoic acid), pyridines (lutidine and picoline), and thiols.

Reaction of SWNTs with TM Compound for the In-Situ Synthesis a TM Catalysts

As an alternative to the reaction of a preformed TMC with a functionalized SWNT, the functionalized SWNT may be reacted with a TM compound or compounds to form the TMC *in situ* on to the end of the SWNT.

As an example, the carboxylate functional groups on the activated SWNT may be reacted with a TM halide to produce a TM complex that will undergo subsequent reaction with other metal containing components. The structure and composition of the resulting TMC will be controlled by the choice of reagents, the reaction conditions, as well as the chirality and diameter of the SWNT. Thus, different TMC can be formed on SWNTs with different characteristics and properties.

A further advantage of this method is that the TMC-SWNTs may be separated based upon the size, charge, coordination chemistry or electrochemistry of the particular TMC. In this manner, SWNTs with different diameters and/or chirality may be separated.

Reaction of the TMC with the SWNT

The reaction of the activated TMC with the functionalized SWNT is carried out under conditions to optimize the formation of the TMC-SWNT complex. The presence of residual TMC and/or SWNT can be used to determine the optimum reaction conditions, and the optimum TMC:SWNT reaction ratio.

As an example, a CHCl_3 solution of the carboxylate functional groups on the activated SWNT may be reacted with an EtOH solution of FeMoC(EtOH) at 55 °C to form a TMC-SWNT complex. If the above is carried out at room temperature, or in DMF, little or no reaction is observed and significant quantities of unreacted FeMoC are observed. These results are summarized in Table 1.

Table 1. Summary of the extent of reaction between FeMoC and SWNTs.

	% FeMoC attached	% SWNTs with FeMoC attached	% Attachment at 2 ends
Room temperature	12	13	0
4 hours @ 55 °C	65	50	11

The optimum TMC:SWNT molar ratio for the reaction will depend on the length of the SWNTs as well as the percentage of SWNTs with activated ends. As an example, functionalized HiPCo SWNTs with an estimated average length of 500 nm are reacted with FeMoC(EtOH) in a 5:1 ratio. Atomic force microscopy (AFM) measurements indicate that essentially all the FeMoC has reacted, but the majority of SWNTs do not show attachment to FeMoC. Performing the reaction with a FeMoC(EtOH):SWNT ratio of 20:1 results in a significant increase in the percentage of SWNTs attached to a FeMoC.

Formation of an Active TMC-SWNT Growth Complex and Growth of the SWNT

It is understood that the TMC-SWNT, as formed by the methods discussed above, is not suitable for the growth of the SWNT directly, but must undergo an activation step to generate unfunctionalized SWNT and an active growth catalyst. This activation step may be performed during the initial stages of SWNT growth or as a separate step.

As an example, the FeMoC must be reduced to yield a suitable particle of Fe/Mo alloy. This reduction may be carried out at elevated temperatures under hydrogen. Heating FeMoC(EtOH) under an inert atmosphere such as nitrogen or argon to ca. 200°C results in the loss of coordinated EtOH and water. Further heating to ca. 370°C results in the elimination of the organic components (e.g., the acetate groups) and strongly complexed water to give a metal oxide particle. Heating this material under hydrogen to ca. 700°C results in the reduction of the metal oxide and the formation of a metal alloy particle and the evolution of water.

In a similar manner, the piranha activated, sidewall functionalized SWNTs must be converted back to unfunctionalized SWNTs. Thermolysis of pir(p)SWNT-C₆H₄-^tBu to 350-400°C under an inert atmosphere yields unfunctionalized SWNTs.

When the TMC-SWNT complex is heated under suitable conditions some part of the SWNT that is attached to the TM alloy particle will be dissolved/reacted with the alloy. As a consequence the TMC and SWNT will remain bound for subsequent SWNT growth.

Conditions for the growth of SWNTs are understood in the literature. Typical conditions include heating the SWNT-FeMoC complex to 700°C under hydrogen.

Formation of a Supported TMC-SWNT Growth Complex

Commercial catalyst systems fall into two general classes: homogeneous and heterogeneous. Heterogeneous catalysts include supported catalysts, where the catalyst is supported on an inert material. Given the low mass of the TMC-SWNT complex, it would be desirable for commercial purposes to use a supported TMC-SWNT. Typical commercial support materials include, but are not limited to, silica, alumina, zeolites, and metal oxides, and combinations thereof.

The supported-TMC-SWNT may be prepared by a number of methods. First the TMC-SWNT complex may be reacted with, or adsorbed onto, a suitable support material. Second the TMC may be reacted with, or adsorbed onto, a suitable support material to which the SWNT is subsequently reacted.

To summarize, FIGURE 2 illustrates, schematically, the attachment of FeMoC to the end of a SWNT (Step 1), the deposition of the SWNT-FeMoC complex on a surface (Step 2), the reductive docking of the FeMoC complex with the SWNT (Step 3), and growth of the SWNT of Step 3 under growth conditions (step 4).

The following Examples are provided to demonstrate particular embodiments of the present invention. It should be appreciated by those of skill in the art that the methods disclosed in the Examples that follow merely represent exemplary embodiments of the present invention. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments described and still obtain a like or similar result without departing from the spirit and scope of the present invention.

EXAMPLES

Example 1

This Example illustrates how SWNTs can be purified, dispersed, and modified for reaction with a TM catalyst.

In a typical procedure, raw carbon nanotubes (as-produced material from the reactor) are first soft-baked by the published procedure (See Liu et al., *Science*, 1998, 280, 1253). This is a purification step, performed to remove exogenous iron and amorphous carbon. The purified carbon nanotubes are then treated with piranha to give carboxylic acid terminated carbon nanotubes. See Liu et al., *Science*, 1998, 280, 1253. The piranha treated carbon nanotubes are

then suspended in water that is facilitated by surfactants. The nanotubes, surfactants and water are added together then homogenized, sonicated, and centrifuged. See O'Connell et al., *Science* 2002, 297, 593. This gives carbon nanotubes that are dispersed in water as predominately individuals. The nanotube solution is then reacted with a diazonium salt, such as $F_4BN_2^+-C_6H_4-tBu$, as described in Dyke et al., *Nano Letters*, 2003, 3, 1215, by adding an excess of an appropriate diazonium salt. The pirhana-treated, functionalized carbon nanotubes are then filtered and washed to remove the excess salt, water, and surfactant. This material [pir(p)SWNT- C_6H_4-tBu] is then resuspended in a suitable solvent to attach a metal cluster to the end of the SWNTs through bonding with the carboxylic acids that terminate the nanotube.

Example 2

This Example serves to illustrate how SWNTs can be surfactant-suspended.

SWNTs (100 mg), purified by wet air oxidation and hexane extracted, are reacted with 50 mL piranha solution (4:1 ratio of conc H_2SO_4 :30% H_2O_2). The reaction mixture is heated to 70°C for 1 hour while stirring. After cooling to room temperature, the mixture is added to nanopure water (200 mL). Filtration, followed by washing with nanopure water (~200 mL), and addition of 1% SDS in nanopure water (200 mL). The suspension is homogenized for 1 hour, then sonicated for 10 minutes, after which the SWNTs are centrifuged (4 hours @ 29,000 rpm). The top 80% is decanted to give a homogeneous solution of surfacted SWNTs.

Example 3

This Example serves to illustrate how surfactant-suspended SWNTs can, once functionalized, be dispersed in another solvent.

The surfactant-suspended SWNT decants of Example 2 were dissolved/suspended in water. After functionalization as in Example 1 to yield pir(p)SWNT- C_6H_4-tBu , these functionalized SWNTs are flocculated upon acetone addition, filtered, and made into "bucky paper" (a solid mat of SWNTs). The bucky paper is then sonicated in the appropriate organic solvent (THF, $CHCl_3$, DMF).

Example 4

This Example serves to illustrate how FeMoC is prepared.

$FeCl_2$ (10 g) is dissolved in water (75 mL). To this solution Na_2MoO_4 (2.0 g) is added, followed by glacial acetic acid (10 mL), $HPMo_{12}O_{40}$ (2.5 g). Once addition is complete the reaction mixture is adjusted to pH 2 with concentrated HCl. This solution is allowed to stand 45 minutes then filtered. Precipitation or evaporation occurs over 2 days in an open flask. The resulting solid is washed with water and the solids dried. EtOH (250 mL, 200 proof) was placed in

a round-bottomed flask (500 mL). Unpurified FeMoC crystals are placed in a filter and then the filter is placed inside the soxhlet thimble. The soxhlet is connected to the round-bottomed flask and also to a condenser on top. The ethanol is refluxed overnight under nitrogen. A concentrated solution of FeMoC in ethanol is collected in the flask while yellow solid keplerate is retained in the filter. The EtOH solution is reduced in volume or to dryness to allow for the isolation of dark green crystals of FeMoC(EtOH). Concentration of FeMoC in ethanol in soxhlet motherliquor: 17.8 mg/mL. Concentration of FeMoC dissolved in EtOH at RT: 12 mg/mL.

Example 5

This procedure outlines the functionalization of the outer surface of FeMoC clusters with molecules of the linker 2-Aminoethanethiol hydrochloride (2-AET·HCl). A 1.8 μ M solution of FeMoC in ethanol was prepared by dissolving 31 mg FeMoC in 1 L of ethanol. A 25 mL aliquot of this cluster solution was placed into an addition funnel. Each FeMoC in the cluster solution is understood to be coordinated with 30 molecules of ethanol, which the 2-AET·HCl linker molecules must displace. For this reason, the concentration of 2-AET·HCl in the ethanolic linker solution should provide 30 molar equivalents of 2-AET·HCl for every single molar equivalent of FeMoC present in the cluster solution. The linker solution was prepared by first dissolving 2-AET·HCl (15.4 mg) in EtOH (100 mL) and then taking a 1 mL aliquot of this solution and diluting the aliquot with ethanol to a final volume of 25 mL. This final linker solution was placed in a round bottom flask, fitted with the addition funnel containing the cluster solution, and set to stir at 80°C. The cluster solution was added dropwise over the course of 15 min. After the addition was complete, the mixture was left stirring at 80°C for an additional 15 min. The solution was then allowed to cool to room temperature. The resultant solution was either used as prepared or the functionalized clusters were isolated from the solvent using room temperature centrifugation at 4400 rpm for 5 min.

Example 6

This Example illustrates a reaction between FeMoC and SWNTs in *N,N*-dimethylformamide (DMF) solvent.

A 5:1 ratio mixture of FeMoC(EtOH) in EtOH and pir(p)SWNT-C₆H₄-^tBu in DMF was allowed to sit at room temperature overnight. The suspension was then spin-coated onto a highly-ordered pyrolytic graphite (HOPG) surface and imaged using AFM.

Example 7

This Example illustrates a reaction between FeMoC and SWNTs in chloroform (CHCl₃).

A 5:1 ratio mixture of FeMoC(EtOH) in EtOH and pir(p)SWNT-C₆H₄-^tBu in CHCl₃ was allowed to react at 55°C for 4 hours. The suspension was spin-coated onto HOPG and imaged using AFM.

Example 8

This Example illustrates a reaction between FeMoC and SWNTs in chloroform (CHCl₃), wherein the reaction mixture comprises more FeMoC(EtOH) in EtOH.

A 20:1 ratio mixture of FeMoC(EtOH) in EtOH and pir(p)SWNT-C₆H₄-^tBu in CHCl₃ was allowed to react at 55 °C for 4 hours. The suspension was spin coated onto HOPG and imaged using atomic force microscopy (AFM), as shown in FIGURES 3 A and B.

All patents and publications referenced herein are hereby incorporated by reference. It will be understood that certain of the above-described structures, functions, and operations of the above-described embodiments are not necessary to practice the present invention and are included in the description simply for completeness of an exemplary embodiment or embodiments. In addition, it will be understood that specific structures, functions, and operations set forth in the above-described referenced patents and publications can be practiced in conjunction with the present invention, but they are not essential to its practice. It is therefore to be understood that the invention may be practiced otherwise than as specifically described without actually departing from the spirit and scope of the present invention as defined by the appended claims.

CLAIMS

What is claimed is:

1. A composition comprising: (a) a suitably functionalized carbon nanotube; and (b) a transition-metal-containing compound attached to the nanotube with a complementary functional group.
2. The composition of claim 1, wherein the carbon nanotube is a single walled carbon nanotube.
3. The composition of claim 1, wherein the transition-metal-containing compound is a catalyst precursor.
4. The composition of claim 1, wherein the transition-metal containing compound is a cluster.
5. The composition of claim 1, wherein the transition-metal-containing compound contains elements selected from the group consisting of iron, chromium, molybdenum, nickel, cobalt, and combinations thereof.
6. The composition of claim 1, wherein the transition-metal-containing compound is a transition metal oxide.
7. The composition of claim 1, wherein the transition-metal-containing compound is FeMoC.
8. The composition of claim 2, wherein the single walled carbon nanotube is side-wall functionalized to inhibit further reaction at the side walls.
9. The composition of claim 2, wherein the single walled carbon nanotube is side-wall functionalized to enhance solubility and separation.
10. The composition of claim 8, wherein the single walled carbon nanotube is side-wall functionalized to prevent roping.

11. The composition of claims 8 or 9, wherein the side-wall functional group moieties are selected from the group consisting of halogen, nitro, cyano, alkyl, aryl, arylalkyl, carboxylic ester, carboxylic acid, thiocarbonate, sulfonate, amide, alkoxy, polyether, hydroxyl, and combinations thereof.
12. The composition of claim 1, wherein the carbon nanotube has been functionalized to allow chemical bonding to the transition metal compound.
13. The composition of claim 1, wherein the transition-metal-containing compound has been functionalized to allow chemical bonding to the carbon nanotube.
14. The composition of claim 12, wherein the carbon nanotube has been functionalized with carboxylate groups.
15. The composition of claim 13, wherein the transition metal compound contains complementary functional groups.
16. The composition of claim 12, wherein the transition metal compound contains leaving groups that allows the reaction between transition metal compound and nanotube to occur.
17. The composition of claim 16, wherein the leaving groups are chosen from the group consisting of methanol, ethanol, alcohol, amine, thiol, ketone, dimethylsulfoxide (DMSO), tetrahydrofuran (THF), and combinations thereof.
18. The composition of claim 1, which is the product from the reaction of the components.
19. A method of making the composition of claim 1 comprising the steps of: (a) functionalizing a nanotube to allow reaction; (b) functionalizing a transition metal compound in a complementary manner; and (c) reacting the SWNT and TM cluster under suitable conditions.
20. A method comprising the steps of: (a) functionalizing a nanotube to protect the side walls from reaction and produce individual nanotube; (b) functionalizing a nanotube to allow reaction; (c) functionalizing a transition metal compound in a complementary manner; and (d) reacting the nanotube and transition metal compound under suitable

conditions to generate carbon nanotubes terminated with functional groups suitable for reaction with transition metal compounds and that disperse as predominately individuals in organic solvent.

21. The method of claim 20, wherein the functional groups are carboxylic acids.
22. A process comprising a coupling reaction between a functionalized nanotube and a transition metal compound.
23. The process of claim 22, wherein the coupling reaction involves acid-base complexation.
24. The process of claim 22, wherein the coupling reaction involves ligand exchange.
25. The process of claim 22, wherein the coupling reaction involves an oxidative addition reaction.
26. The process of claim 22, wherein the coupling reaction involves a condensation reaction.
27. A composition of matter comprising: (a) a suitably functionalized carbon nanotube; (b) a transition metal containing compound attached to the nanotube with a complementary functional group; and (c) a suitable support material.
28. The composition of claim 27, wherein the carbon nanotube is attached to the support.
29. The composition of claim 27, wherein the transition metal compound is attached to the support.
30. The composition of claim 27, wherein the support is used as a catalyst support for the growth of nanotubes.
31. The composition of claim 27, wherein the surface may be functionalized prior to the coupling.

32. The composition of claim 27, wherein the transition metal compound may be functionalized prior to the coupling.
33. A process comprising: (a) reacting a carbon nanotube with a transition metal compound; and (b) heating the product from the reaction between the carbon nanotube and the transition metal compound under conditions to convert the functionalized nanotube to an unfunctionalized nanotube.
34. A process comprising: (a) reacting a carbon nanotube with a transition metal compound; (b) heating the product from the reaction between the carbon nanotube and the transition metal compound under conditions to convert the functionalized nanotube to an unfunctionalized nanotube; and (c) converting the transition metal compound to a transition metal particle or alloy particle.
35. A process of claim 34, further comprising a step of exposing to a reagent that allows growth of the nanotube.
36. A process according to claim 34 where the new growth of the tube matches the predetermined pattern of the original tube type (same m and n as that possessed by the original tube).

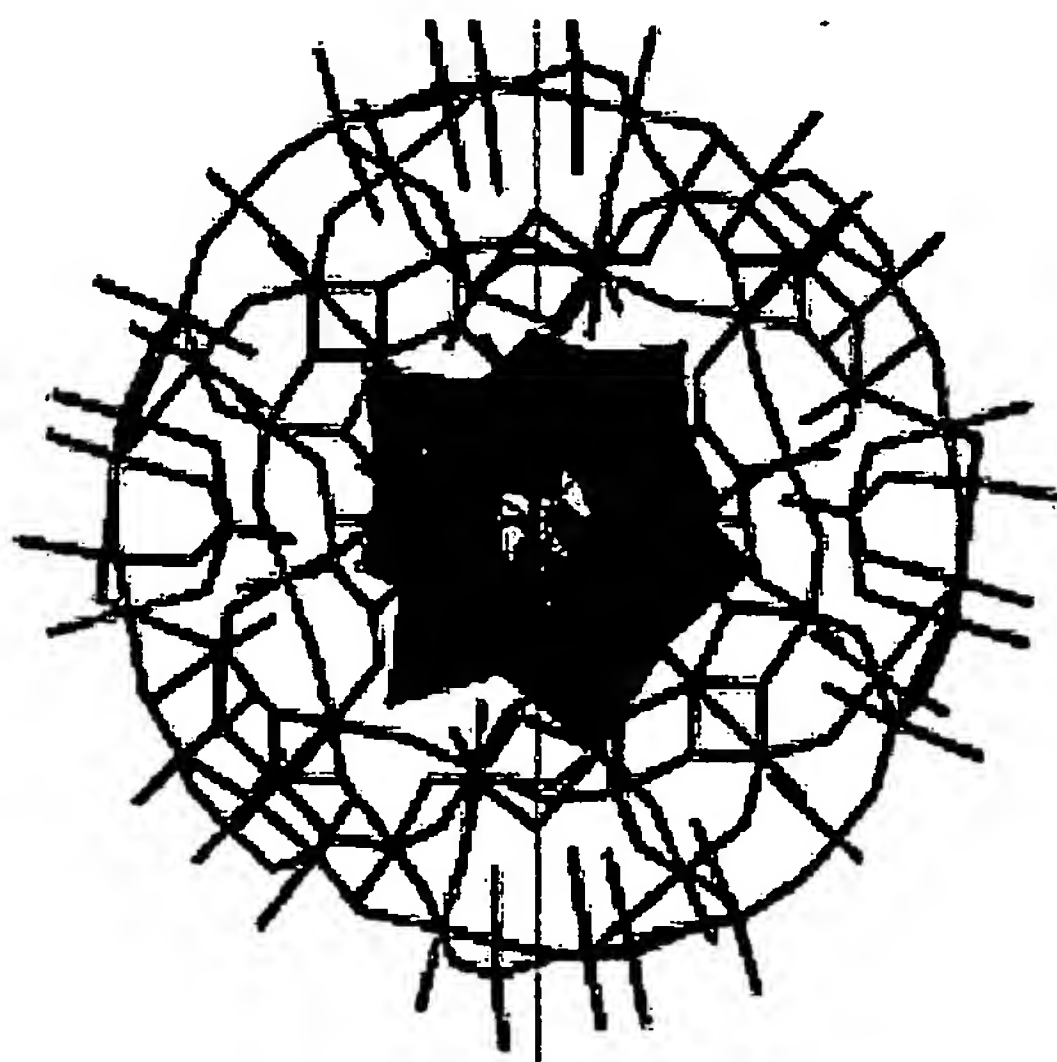
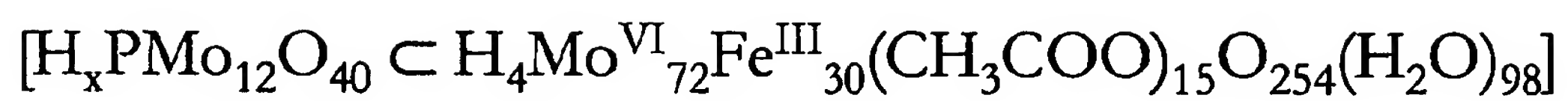
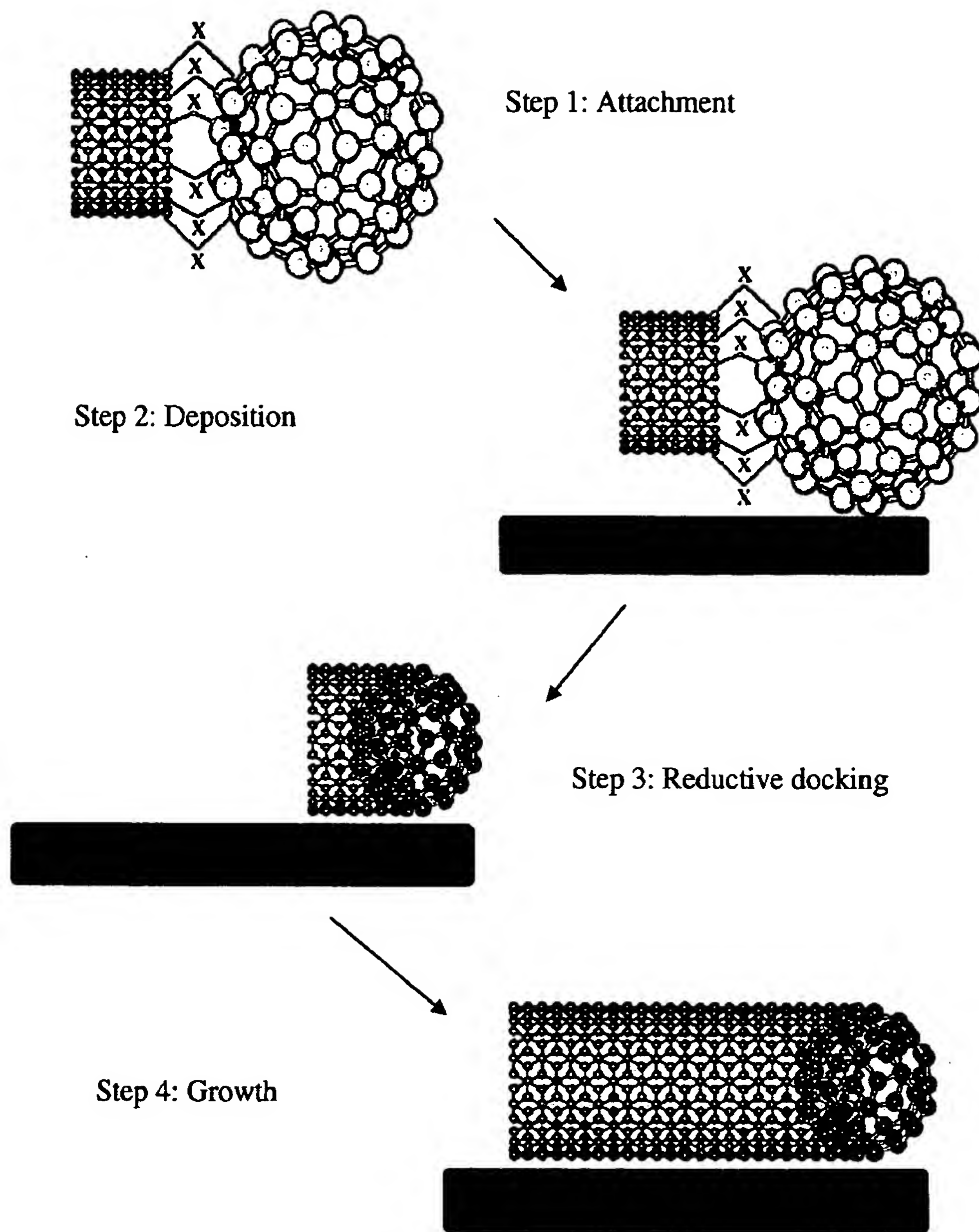


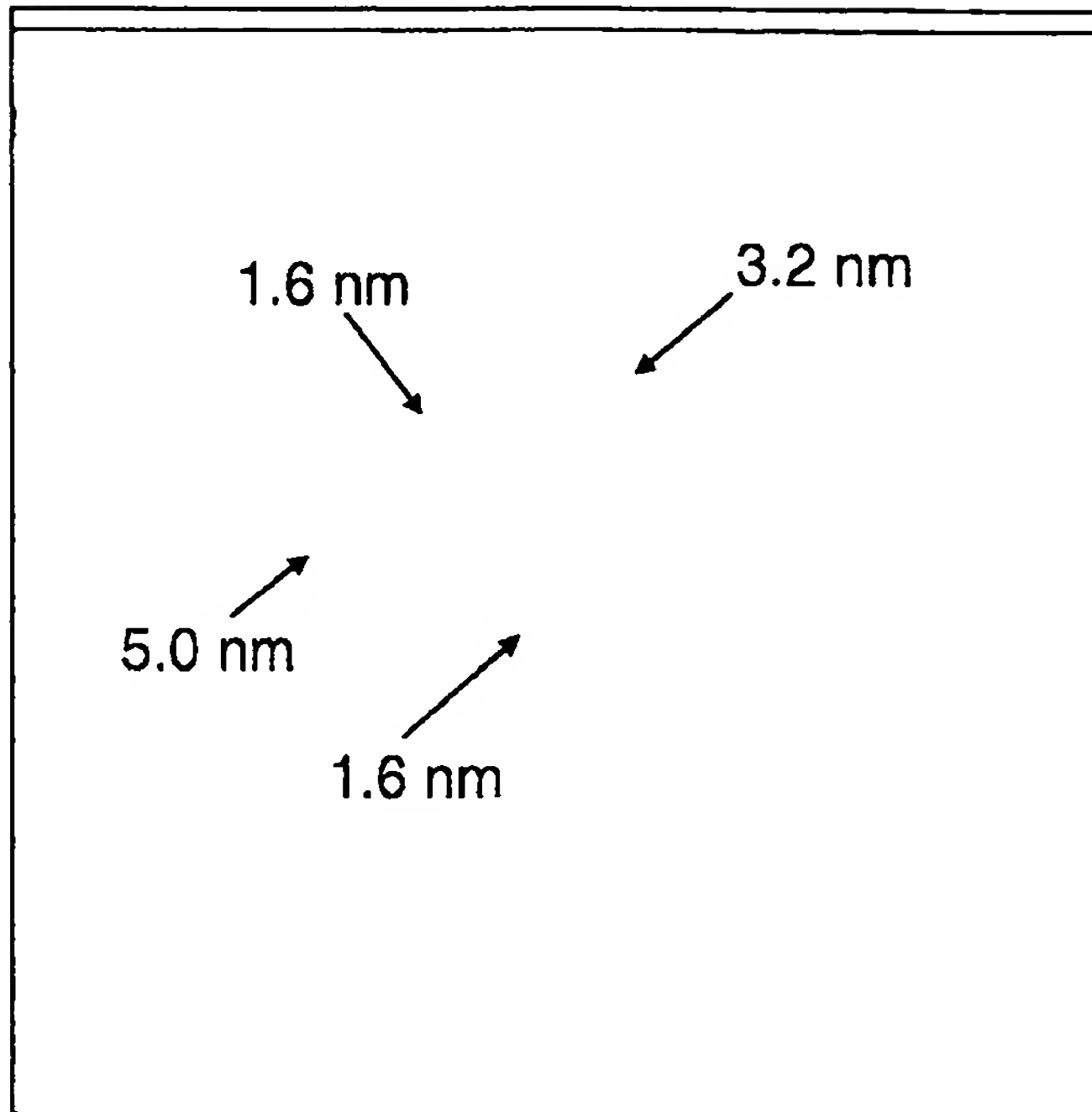
Fig. 1



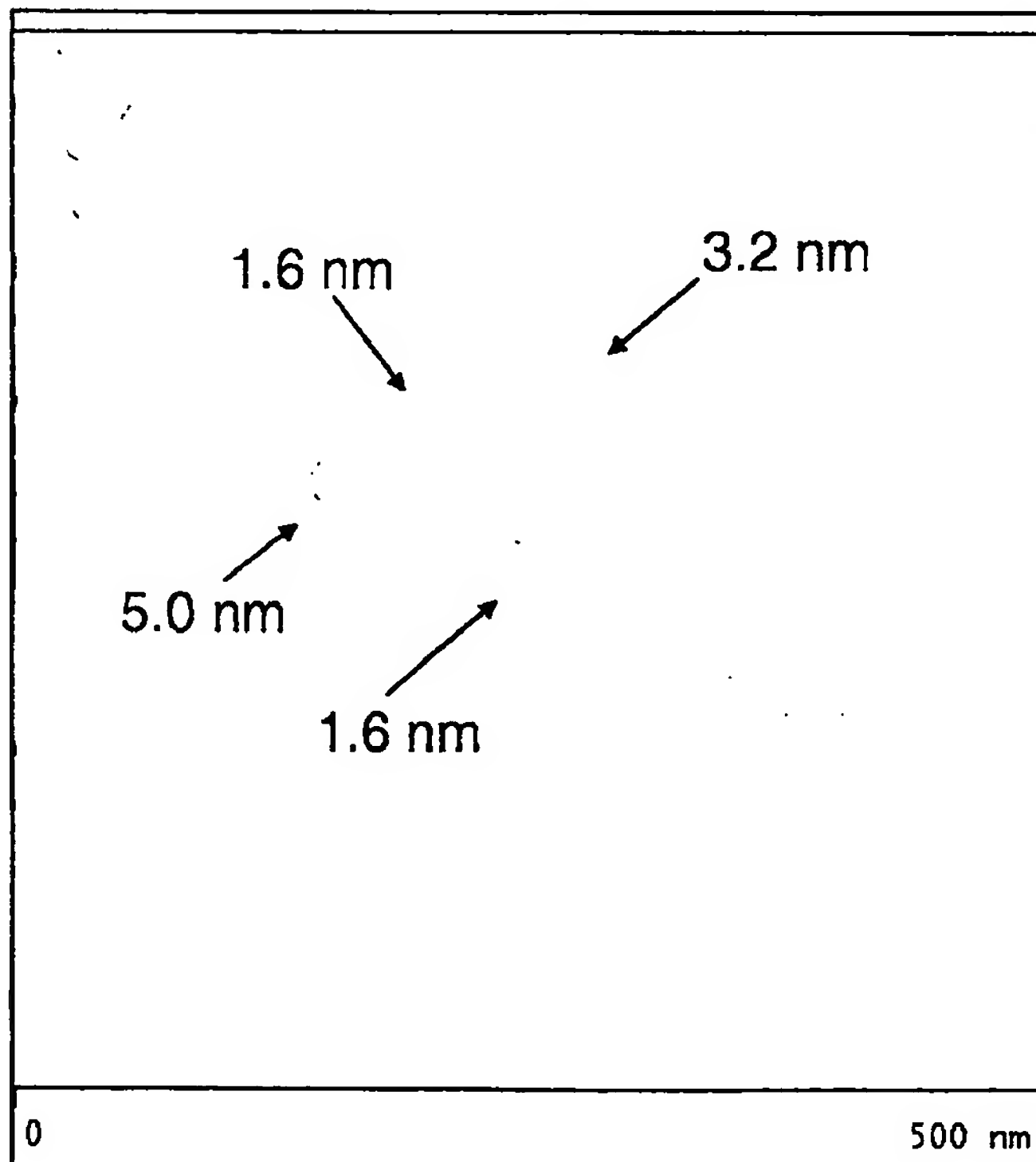
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Fig. 2

A



B



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Fig. 3

Application Data Sheet**Application Information**

Application number::	To be assigned
Filing Date::	July 12, 2004
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Suggested Group Art Unit::	
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